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DISSOCIATION CONSTANTS OF MALONIC ACID IN ITS SODIUM-SALT SOLUTIONS AT 25° C FROM ELECTROMETRIC TITRATION MEASUREMENTS

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ABSTRACT

Electrometric titration of 0.1 *M* malonic acid by 0.1007 *N* sodium hydroxide was completed at 25° C for the determination of the pH titration curve and the calculations of the primary and secondary dissociation constants. The treatment of the data embodied the application of the Henderson equation for liquid-junction potential, the Debye-Hückel theory of interionic attraction, and the Guggenheim-Hückel expression for the variation of the ionic activity coefficients with concentration. The dissociation constants found for malonic acid at 25° C are $K_1=2.06\times10^{-3}$ and $K_2=2.94\times10^{-6}$.

CONTENTS

	Page
I. Introduction.....	575
II. Experimental measurements.....	576
1. Apparatus.....	576
2. Materials.....	577
3. Procedure.....	577
III. pH determinations.....	578
IV. pH titration curve.....	583
V. Calculation of the dissociation constants.....	585
VI. Calculation of the intermediate range.....	587
VII. Discussion.....	588
VIII. Summary.....	591
IX. References.....	592

I. INTRODUCTION

Dibasic organic acids are, in general, found in the oxidized portions of natural sugars. As an aid in the interpretation of the oxidation and analysis of the product, accurate values of the dissociation constants of the acids are desired. In this paper malonic acid is considered. Previous values reported (at 25° C) for this acid by investigators [1],² who employed widely different methods, vary from 1.40×10^{-3} to 2.11×10^{-3} for the first ionization constant and from 1.36×10^{-6} to 10.0×10^{-6} for the second. Part of this divergence is due to the use of classical dilution laws and neglect of interionic attrac-

¹ This paper includes data presented in a dissertation submitted by John O. Burton to the Faculty of the Graduate School of the University of Maryland, represented by Prof. M. M. Haring of the Department of Chemistry, in partial fulfillment of the requirements for the degree of Master of Science.

² The numbers in brackets here and throughout the text refer to the numbered references at the end of this paper.

tion theories developed by Milner [2] and by Debye and Hückel, [3] and, in part, to assumptions that the sodium salts of malonic acid have colligative properties similar to those of the sodium salts of other monobasic and dibasic acids. In this paper the electrometric titration of malonic acid by sodium hydroxide is presented, and the data are treated with the use of the interionic attraction theory and

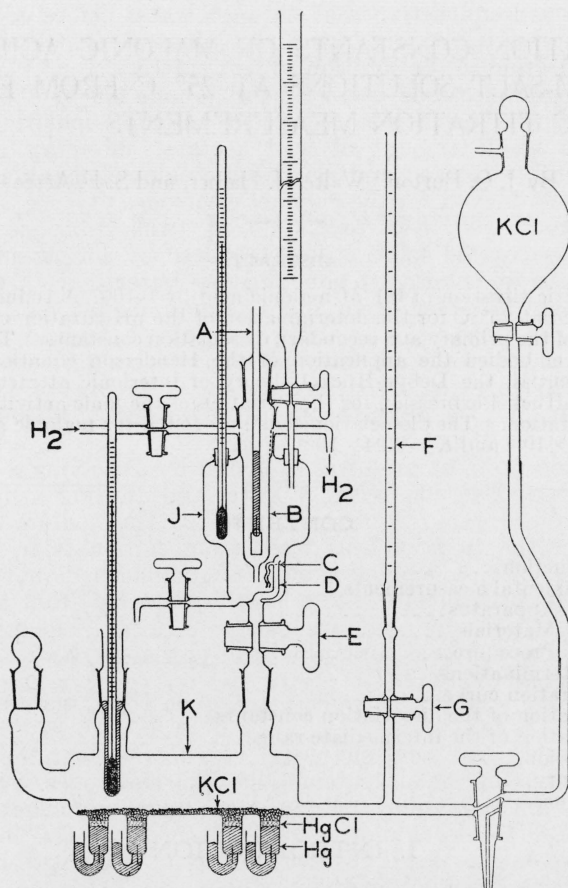


FIGURE 1.—Hydrogen and calomel electrodes for making pH titrations.

independently of assumptions as regards structural and colligative identity with other salts.

II. EXPERIMENTAL MEASUREMENTS

1. APPARATUS

The pH measurements were made with a hydrogen electrode in an electrode vessel, as shown in figure 1. The reference electrode consisted of a battery of four saturated calomel electrodes, K. These were brought to constant potential with each other by short-circuiting as recommended by Loomis and Acree [4]. The electromotive-force

measurements were made with a Leeds and Northrup type K potentiometer and 2500-e galvanometer, with lamp and scale. The titrations were made in an air thermostat, controlled at 25° C to within $\pm 0.2^\circ$ C.

2. MATERIALS

Tank hydrogen, purified from oxygen by passing through a tube containing palladinized asbestos heated to 220° C, was employed. The gas was subsequently passed through water before admission to the titration vessel, in order to insure against concentration changes due to evaporation in the solution to be titrated.

The hydrogen electrode was gold foil (about 0.5 by 1 cm) plated with palladium black from a 3 percent palladous chloride solution containing a small amount of lead acetate. Mercury cleaned in nitric acid and redistilled and electrolytic calomel manufactured by Eppley were employed for the calomel electrodes.

Potassium chloride was recrystallized twice from conductivity water. The saturated solution was prepared by adding an excess of purified potassium chloride to conductivity water.

Malonic acid obtained from the Eastman Kodak Co., was used without further purification. A dried sample of the acid neutralized the theoretical amount of standard alkali to within 0.1 percent, which corresponds to an error of approximately ± 0.1 mv, or an error of ± 0.3 percent in pH, provided that the impurity is untitratable, which is probably the case.

The solution to be titrated was prepared by dissolving a calculated weight of dry acid in conductivity water and diluting to the desired volume in a calibrated Pyrex-glass flask. The sodium hydroxide employed for the titration was freed from carbonate by preparing the saturated solution, siphoning off the supernatant liquid above the insoluble sodium carbonate into a bottle protected from the atmosphere by soda-lime tubes, and diluting to 0.10 *N*. The solution was then standardized against potassium acid phthalate, National Bureau of Standards Sample 84.

3. PROCEDURE

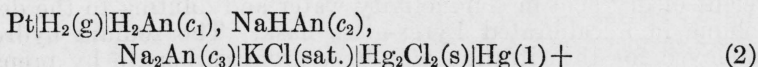
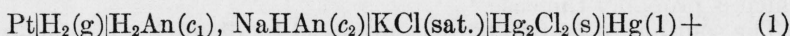
The apparatus and solutions were placed in the air thermostat 2 hours before making the measurements. The electrodes were checked against an 0.05 *N* potassium acid phthalate buffer immediately before the titration. The electromotive force obtained was 0.4796 at 25° C, which corresponds to a pH of 3.96, and is in good agreement with 3.97 obtained by Clark [5] for this buffer.

Twenty-five milliliters of the acid was then pipetted into the titration vessel. Stopcock E was then opened and solution contact was made by gently raising the level of the saturated potassium chloride to C by admitting the potassium chloride solution from the reservoir, at which point, C, a diffusion junction was formed. This type of junction is considered to be the better type for a junction between solutions of different electrolytes, whether they are of like or unlike valence type [6]. Stopcock E was then closed, and hydrogen was passed over the electrode and through the solution. After the hydrogen had bubbled for 3 minutes, tube B was rotated through an angle of 180 degrees to force solution into B and make contact with the electrode, the hydrogen was turned off, stopcock E opened, and a liquid junction was made as described before. The electromotive

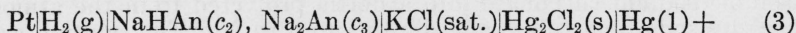
force was then recorded. This procedure was repeated until successive readings of electromotive force agreed to within ± 0.2 mv. After the electromotive force was found to be constant within this limit, standard sodium hydroxide solution was added by means of the burette, and the new electromotive force was obtained by repetition of the procedure outlined above. It was found that for the first measurement it was necessary to pass hydrogen through the solution several times for 3 minutes each, before a constant potential could be obtained. Subsequent measurements were found to be constant after passing the hydrogen through the solution for 3 minutes, except near the end of the pH titration curve, where the pH was changing rapidly. However, for each point on the curve the hydrogen was bubbled for at least two 3-minute periods. The temperatures in the titration vessel and calomel electrode were checked frequently throughout the titration and always were found to agree within $\pm 0.1^\circ \text{C}$ with each other and the temperature reported for the titration. The electromotive forces were corrected to one atmosphere hydrogen pressure, as recommended by Acree and coworkers [7].

III. pH DETERMINATIONS

In the electrometric titration of malonic acid with sodium hydroxide, the three galvanic cells



and



are, in reality, measured. Cell 1 corresponds to the first part of the titration during which neutralization of the first acid group (HAN^-) occurs; cell 2 to the intermediate range, where both groups (HAN^- and An^-) are simultaneously neutralized; and cell 3 to the final range, in which only the second group (An^-) is titrated. The parallel lines indicate separate phases, and the commas are employed to indicate different components within one phase, as is the convention adopted by the International Critical Tables [8]. "An", abbreviation for anion, is employed to represent the malonate ion, and "HAN" to represent the acid malonate ion. The measured electromotive forces of these three cells are all given by the semi-thermodynamic equation

$$E = E_0 + E_1 - \frac{RT}{F} \ln c_{\text{H}} f_{\text{H}}, \quad (4)$$

where E is the measured electromotive force; E_0 the normal electrode potential of the reference electrode $\text{Hg}(1) \text{Hg}_2\text{Cl}_2(\text{s}) \text{KCl}(\text{sat.})$; E_1 the liquid-junction potential at the boundary, acid, salts| $\text{KCl}(\text{sat.})$; c_{H} the hydrogen-ion concentration, in moles per liter; and f_{H} the practical activity coefficient of the hydrogen ion, respectively.

The liquid-junction potential E_1 is equal to the sum of the diffusion potential E_{D} and the activity potential E_{A} , which corrects for the

deviations of E_D from the classical dilution laws due to interionic attraction. Upon substitution and rearrangement, the equation

$$(E - E_0 - E_D)/0.05915 - E_t/0.05915 + \log f_H = -\log c_H = \text{pH} \quad (5)$$

results, where the numerical value of $RT/2.3026F$ at 25°C is 0.05915. Since E , the measured value, and E_0 , which has been shown by Scatchard [9] to be equal to 0.2454 volt, are the only values obtained directly by experiment, it is necessary to evaluate E_D , $E_t/0.05915$, and $\log f_H$ in order to obtain values for the hydrogen-ion concentration or pH . The former two are given by the integrals [10]

$$E_D = - \sum_1^p 0.05915 \int_1^2 t_i d \ln c_i, \quad (6)$$

$$E_t = - \sum_1^p 0.05915 \int_1^2 t_i d \ln f_i, \quad (7)$$

and their sum E_j by

$$E_j = - \sum_1^p 0.05915 \int_1^2 t_i d \ln a_i, \quad (8)$$

where the limits 1 and 2 refer to solution (sat. KCl) and solution (acid-salt), respectively, and t_i represents the ionic transference number and a_i the ionic activity of the ions involved in the transfer of electrolyte at the boundary. The integral refers to an individual ion, but the sum is for all the ions involved, p .

Henderson [11] arrived at a solution of equation 6 by assuming an initial mixing of the solutions at a sharp boundary. His solution gives, respectively, for cells 1, 2, and 3 the following equations:

$$E_D = - (RT/F) \frac{c_s(U_s - V_s) - c_H U_H - c_2(U_2 - V_2)}{c_s(U_s + V_s) - c_H U_H - c_2(U_2 + V_2)} \ln \frac{c_s(U_s + V_s)}{c_H U_H + c_2(U_2 + V_2)} \quad (9)$$

$$E_D = - (RT/F) \frac{c_s(U_s - V_s) - c_H U_H - c_2(U_2 - V_2) - c_3(U_3 - V_3)}{c_s(U_s + V_s) - c_H U_H - c_2(U_2 - V_2) - c_3(U_3 - V_3)} \ln \frac{c_s(U_s + V_s)}{c_H U_H + c_2(U_2 + V_2) + c_3(U_3 + V_3)} \quad (10)$$

$$E_D = - (RT/F) \frac{c_s(U_s - V_s) - c_H U_H - c_3(U_3 - V_3)}{c_s(U_s + V_s) - c_H U_H - c_3(U_3 + V_3)} \ln \frac{c_s(U_s + V_s)}{c_H U_H + c_3(U_3 + V_3)}, \quad (11)$$

where c_s is the concentration of saturated potassium chloride (4.13 N); U refers to cationic mobility; and V to anionic mobility of the salts denoted by the same subscripts as were employed in the formulation of cells 1, 2, and 3. Numerical values of the mobilities are U_s [12] = 73.50; V_s [12] = 76.32; U_H [12] = 349.72; $U_2 = U_3$ [12] = 50.10; V_2 [13] = 35.5; V_3 [14] = 63.0 (corrected by 0.014 percent for error in cell constant of Kohlrausch's [15] conductance measurements),

and values of c_2 and c_3 are obtained from the stoichiometrical concentrations of NaHAn and Na_2An , which are given in columns 6 and 7 of table 1, and from the hydrogen-ion concentration found prior to liquid-junction corrections.

Values of E_D calculated by equations 9 and 11 are given in column 3 of table 2. These calculations are for the treatment of malonic acid and its acid salt as monobasic acids. For the intermediate range where the acid is treated as a dibasic acid equation 10 is employed. Values calculated by its use are given in column 2 of table 3. The corrections produced by the use of E_D give new values of the hydrogen-ion concentration, c_H . These new values of c_H are then substituted in the above equations and the process repeated until values of c_H and E_D are consistent with each other. In this work only one calculation was found necessary for consistency, owing to the low magnitude of c_H , the hydrogen-ion concentration.

TABLE 1.—*Stoichiometrical concentrations prevailing in the titration of 25 milliliters of 0.10 M malonic acid by 0.1007 N sodium hydroxide*

0.1007 N NaOH	Moles NaOH per mole acid	J=equiv. conc. of Na salts	$M_{\text{H}_2\text{An}}$	$M_{\text{H}_2\text{An}} = U$	M_{NaHAn}	$M_{\text{Na}_2\text{An}}$
ml						
0.00	0.000000	0.000000	0.100000	0.100000	0.000000	-----
1.00	.040285	.003873	.096154	.092281	.003873	-----
2.06	.08299	.007666	.092387	.084721	.007666	-----
3.21	.12931	.011459	.088621	.077162	.011459	-----
4.26	.17161	.014661	.085437	.070776	.014661	-----
5.11	.20586	.017090	.083029	.065939	.017090	-----
6.10	.24574	.019751	.080386	.060637	.019751	-----
7.12	.28683	.022322	.077833	.055511	.022322	-----
9.10	.3666	.026873	.073314	.046441	.026873	-----
11.08	.4464	.030925	.069290	.038365	.030925	-----
13.10	.5277	.034624	.065627	.031003	.034624	-----
15.10	.6083	.037919	.062344	.024423	.037919	-----
17.10	.6889	.040902	.059382	.018480	.040902	-----
19.10	.7694	.043614	.056690	.013076	.043614	-----
20.10	.8097	.044880	.055432	.010552	.044880	-----
21.10	.8500	.046090	.054230	.008140	.046090	-----
22.10	.8903	.047248	.053079	.005831	.047248	-----
23.14	.9322	.048405	.051930	.003525	.048405	-----
23.66	.9531	.048964	.051377	.002413	.048964	-----
24.25	.9769	.049583	.050761	.001178	.049583	-----
24.86	1.00148	.050209	.050209	.000000	.050209	0.000000
25.36	1.02162	.050710	.049642	-----	.048574	.001068
25.86	1.04177	.051202	.049155	-----	.047108	.002047
26.35	1.06151	.051674	.048685	-----	.045696	.002959
27.40	1.10380	.052656	.047710	-----	.042764	.004946
28.35	1.14208	.053512	.046861	-----	.040210	.006651
29.35	1.18236	.054380	.045998	-----	.037616	.008382
30.39	1.22426	.055250	.045135	-----	.035020	.010115
31.85	1.28307	.056417	.043975	-----	.031533	.012442
33.85	1.36364	.057922	.042481	-----	.027040	.015441
35.85	1.44421	.059328	.041085	-----	.022842	.018243
37.85	1.52478	.060644	.039777	-----	.018910	.020867
39.85	1.60535	.061880	.038551	-----	.015222	.023329
41.85	1.68662	.063040	.037398	-----	.011756	.025642
42.85	1.72631	.063600	.036846	-----	.010092	.026754
43.83	1.76578	.064128	.036321	-----	.008514	.027807
44.83	1.80607	.064652	.035802	-----	.006952	.028850
45.83	1.84635	.065161	.035296	-----	.005431	.029865
46.83	1.88664	.065655	.034804	-----	.003953	.030861
47.58	1.91685	.066017	.034445	-----	.002873	.031571
48.08	1.93699	.066255	.034209	-----	.002163	.032046
48.58	1.95714	.066489	.033977	-----	.001465	.032512
48.84	1.96761	.066609	.033857	-----	.001105	.032752
49.10	1.97809	.066729	.033738	-----	.000747	.032991
49.35	1.98816	.066843	.033625	-----	.000407	.033218
49.61	1.99863	.066961	.033508	-----	.000055	.033453
49.84	2.00790	.067065	.033404	-----	-----	.033661

Since no functional or analytical expression is known which defines a relation between t_1 and f_1 , it is necessary to resort to graphical integration to evaluate E_t . This may be done by the method suggested by Harned [16]. In this, transference numbers of each ion involved at the junction are calculated for various mixtures between saturated potassium chloride and the titrated solution, assuming uniform mixing of the solutions at the boundary. Then these values of t_1 are each plotted against $\log f_1$ of the acid-salt mixtures, employing the law of the linear variation of activity coefficients at constant total molality [17], and the area under the integral is evaluated by counting the squares. For instance, after 1.00 cm³ of alkali has been added, this integral equals -0.00203 . Details and further discussion are omitted for reasons to be given in the following paragraph.

The magnitude of f_H remains to be determined. For dilute solutions these values may be calculated from data on pure hydrochloric acid and pure potassium chloride. First the values of the activity coefficients for potassium chloride obtained by Robinson and Sinclair [18] are employed. Since the mobilities of the ions of this salt are nearly the same [12] their activity coefficients are taken as equal. Then the mean activity coefficients of hydrochloric acid obtained by Harned and Ehlers [19] or by Randall and Young [20] are squared and divided by the activity coefficient of the chloride ion, which gives the activity coefficient of the hydrogen ion at the same concentration for which the values of potassium chloride and hydrochloric acid were used. This procedure embodies the assumption that the activity coefficient of an ion is uninfluenced by the ion with which it is associated, and in dilute solutions this is very nearly the case. For instance, the mean activity coefficient at 0.01 *N* for hydrochloric acid [19, 20] is 0.904 and for potassium chloride [18] it is 0.903. This procedure for the calculations of the activity coefficient of the hydrogen ion is that proposed by MacInnes [21] and employed by others [22], except that, in this case, the calculations were made in terms of normality and not in terms of molality as was done by MacInnes. The activity coefficients obtained by Robinson and Sinclair and by Harned and Ehlers for potassium chloride and hydrochloric acid were consequently corrected to the normality basis by multiplying their values by the ratio of molality to normality. Values of f_H thus calculated are given in column 9 of table 2. A comparison of the magnitude of E_t and $\log f_H$ may now be made. From table 2 the value of f_H after the addition of 1.00 ml alkali is found to be 0.893. The logarithm of this value multiplied by 0.05915, since $E_t = 0.05915 \log f_H$, gives 0.00291. E_t at the same point was found above to be 0.00203, hence E_t is *approximately* equal to $0.05915 \log f_H$ in value.* At this point of the titration the hydrogen-ion concentration has its highest value (first point excepted).

Therefore, this difference in E_t and $0.05915 \log f_H$ becomes even less as the titration proceeds. Since the difference observed is beyond

* The relative nature of this treatment has been clearly defined by Harned, *J. Phys. Chem.* **30**, 499 (1926).

the experimental error these two quantities may be taken as exactly equal, and equation 5 is then written in the form

$$(E - E_0 - E_D)/0.05915 = \text{pH} = -\log c_H. \quad (12)$$

Values of pH calculated by this equation are given in table 2, column 4.

TABLE 2.—Data for titration of 0.10 M malonic acid at 25° C as a monobasic acid

FIRST EQUIVALENT OF SODIUM HYDROXIDE

0.1007 N NaOH	<i>E</i>	<i>E_D</i> ×10 ⁴	pH	<i>c_H</i> ×10 ⁸	<i>n</i>	<i>K</i> ₁ ^c ×10 ³	<i>μ</i>	<i>f_H</i>	<i>K</i> ₁ ^a ×10 ³
ml	<i>Volts</i>	<i>Volts</i>							
0.00	0.3569	34	1.83	1.4860	2	2.56	0.022290	0.887	1.95
1.00	.3603	32	1.89	1.2942	2	2.74	.023286	.893	2.10
2.06	.3648	31	1.97	1.0815	2	2.70	.023829	.901	2.08
3.21	.3695	30	2.05	8.974	3	2.69	.024920	.909	2.09
4.26	.3736	30	2.12	7.638	3	2.70	.026118	.915	2.10
5.11	.3771	30	2.18	6.668	3	2.67	.027092	.920	2.08
6.10	.3808	29	2.24	5.754	3	2.67	.028382	.925	2.09
7.12	.3848	29	2.31	4.920	3	2.65	.029702	.929	2.08
9.10	.3922	28	2.43	3.681	3	2.63	.032395	.938	2.06
11.08	.3997	28	2.56	2.748	3	2.60	.035047	.945	2.04
13.10	.4074	27	2.69	2.028	3	2.57	.037666	.952	2.03
15.10	.4153	27	2.83	1.489	3	2.56	.040153	.959	2.02
17.10	.4239	27	2.97	1.067	3	2.57	.042503	.965	2.03
19.10	.4343	26	3.15	7.080	4	2.54	.044676	.970	2.01
20.10	.4401	26	3.25	5.662	4	2.58	.045729	.973	2.05
21.10	.4468	26	3.36	4.355	4	2.63	.046744	.976	2.09
22.10	.4541	26	3.48	3.281	4	2.84	.047740	.979	2.26
23.14	.4633	26	3.64	2.291	4	3.38	.048749	.982	2.69
23.66	.4688	26	3.73	1.849	4	4.12	.049241	.983	3.28
24.25	.4747	26	3.83	1.469	4	7.09	.049241	.986	5.66

SECOND EQUIVALENT OF SODIUM HYDROXIDE ¹

						<i>K</i> ₂ ^c ×10 ⁶			<i>K</i> ₂ ^a ×10 ⁶
24.86	0.4814	23	3.95	1.1195	4	0.25	0.050489	0.987	0.13
25.36	.4865	23	4.04	9.1833	5	2.20	.052007	.989	1.14
25.86	.4916	23	4.12	7.5335	5	3.40	.053437	.991	1.75
26.35	.4961	23	4.20	6.3241	5	4.23	.054821	.992	2.16
27.40	.5049	23	4.35	4.4874	5	5.27	.057714	.993	2.66
28.35	.5118	23	4.47	3.4276	5	5.70	.060249	.994	2.85
29.35	.5183	24	4.57	2.6730	5	6.01	.062829	.996	2.97
30.39	.5242	24	4.67	2.1232	5	6.15	.065418	.996	2.98
31.85	.5319	24	4.80	1.5740	5	6.22	.068898	.997	3.00
33.85	.5411	25	4.96	1.1041	5	6.31	.073396	.998	2.99
35.85	.5497	25	5.10	7.9068	6	6.32	.077591	.999	2.95
37.85	.5581	25	5.24	5.7016	6	6.30	.081525	.999	2.89
39.85	.5667	26	5.39	4.0926	6	6.28	.085219	1.0	2.85
41.85	.5763	26	5.50	2.8184	6	6.15	.088689	1.0	2.76
42.85	.5815	26	5.64	2.3015	6	6.10	.090360	1.0	2.72
43.83	.5871	26	5.73	1.8493	6	6.04	.091940	1.0	2.68
44.83	.5938	27	5.84	1.4322	6	5.95	.093506	1.0	2.62
45.83	.6020	27	5.98	1.0400	6	5.72	.095079	1.0	2.51
46.83	.6127	27	6.16	6.8550	7	5.35	.096508	1.0	2.34
47.58	.6243	27	6.36	4.3652	7	4.80	.097587	1.0	2.09

¹ Since *K*₂^a drops rapidly near the end of the titration, owing to rapid change in pH, which magnifies the experimental error, these values have not been incorporated into the table. From 47.58 ml of added alkali to end of the titration, the electromotive forces are, respectively, for the milliliter of added alkali listed in table 1: 0.6352, 0.6556, 0.6734, 0.7143, 0.7715, 0.8069, and 0.8310 volt, and *E_D* is 0.0027 volt for all. The corresponding pH values are, respectively, 6.54, 6.89, 7.19, 7.88, 8.85, 9.45, and 9.86.

TABLE 3.—Data for titration of 0.10 *M* malonic acid at 25° C as a dibasic acid

0.1007 <i>N</i> NaOH	$E_D \times 10^4$	$CH \times 10^n$	η	$CNa_2An \times 10^6$	$CNaHAn$	$CH_2An \times 10^6$	μ	$K_1^a \times 10^3$	$K_2^a \times 10^6$
ml									
17.10	27	1.067	3	-----	0.04597	17411	0.042503	^a 2.03	-----
19.10	26	7.080	4	-----	.04432	12372	.044676	^a 2.01	-----
20.10	26	5.662	4	-----	.04545	9984	.045729	^a 2.05	-----
21.10	26	4.355	4	644	.04598	761	.04813	2.08	3.17
22.10	25	3.266	4	867	.04643	579	.04919	2.08	3.17
23.14	25	2.280	4	1248	.04665	404	.05051	2.09	3.16
23.66	25	1.841	4	1543	.04657	327	.05129	2.08	3.14
24.25	25	1.466	4	1924	.04624	260	.05209	2.09	3.14
24.86	25	1.127	4	2474	.04572	195	.05319	2.09	3.12
25.36	25	9.247	5	2974	.04508	158	.05410	2.10	3.12
25.86	25	7.586	5	3563	.04431	128	.05504	2.09	3.11
26.35	25	6.368	5	4164	.04347	106	.05603	2.09	3.10
27.40	25	4.519	5	5589	.04140	72	.05819	2.08	3.07
28.35	25	3.452	5	6959	.03938	52	.06028	2.08	3.04
29.35	25	2.686	5	8347	.03727	38	.06232	2.07	3.02
30.39	25	2.133	5	9836	.03504	29	.06452	2.07	2.99
31.85	24	1.574	5	12943	.03104	-----	.068898	-----	^a 3.00
33.85	25	1.1041	5	15462	.02701	-----	.073396	-----	^a 2.99
35.85	25	7.9068	6	18260	.02253	-----	.077591	-----	^a 2.95

^a Values obtained by the monobasic treatment.

IV. pH TITRATION CURVE

In figure 2 the titration curve of 0.10 *M* malonic acid with 0.1007 *N* sodium hydroxide is shown graphically by curve C. Since the stoichiometrical concentrations of malonic acid, sodium acid malonate, and disodium malonate may each be calculated from the stoichiometrical equations for each volume formed by the addition of alkali, and the total concentration of the acid is known, the mole fraction of each may be obtained. Curve A shows the change of the mole fraction of sodium acid malonate with pH; curve D the change of the mole fraction of disodium malonate with pH. Curve B is 1 minus the mole fraction of un-ionized acid, thus showing the amount of acid ionized and titrated at each pH value. For curve A and B, therefore, the abscissas, given as moles NaOH per mole acid, can also be read between 0 and 1.0 as mole fractions of sodium acid malonate present and of acid titrated or ionized. If the abscissas are read as 1 less than the value given between 1.0 and 2.0, they will then indicate the mole fractions of disodium malonate. In this figure the pH values plotted are those obtained without liquid-junction corrections, so that a comparison with those obtained with such corrections may be briefly made. The liquid-junction corrections merely displace all these curves by approximately -0.06 pH unit. This emphasizes the fact that for the determination of absolute values, corrections for liquid junction are essential, but no large effect is introduced for percentage determinations. Consequently, in routine work if only percentage change is desired, the liquid-junction corrections may be omitted.

Values of the moles of NaOH per mole malonic acid and the stoichiometrical concentrations of added alkali (total equivalent concentration of Na salts= J), total acid, and unneutralized acid are given in table 1, columns 2, 3, 4, and 5, respectively. Stoichiometrical concentrations of the sodium acid malonate and disodium malonate ions are given in the same table in columns 6 and 7, respectively. The ionic concentration of the hydrogen ion is given in column 5 of table 2 and column 3 of table 3. If M represents stoichiometrical concentra-

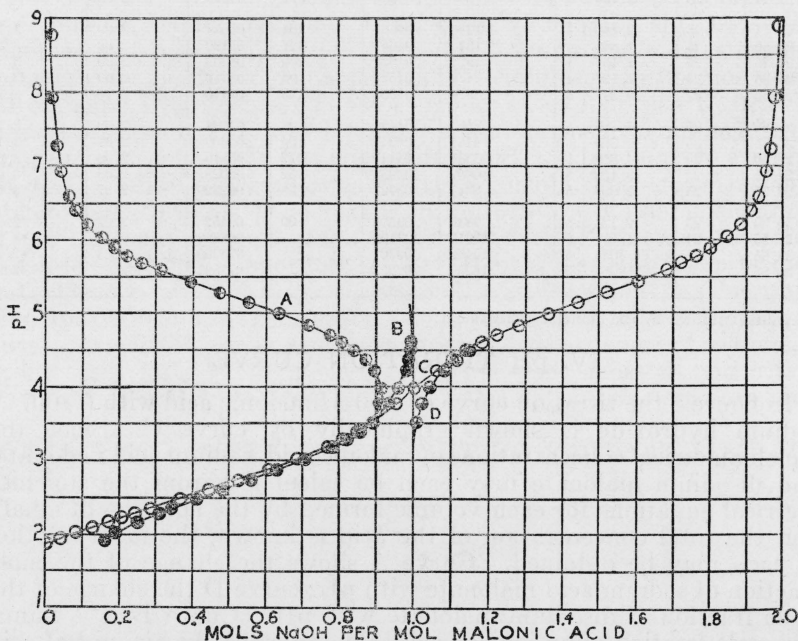


FIGURE 2.—Change of composition of malonic acid solution with pH.

- A. Mole fractions monosodium salt = ● and ○ below 0.9 mole NaOH.
 B. Mole fraction total ionized and titrated acid = ⊙
 C. pH titration curve = ○
 D. Mole fraction disodium salt = ⊖

tions and c ionic concentrations, the following equations define their relation throughout the titration:

$$c_{\text{NaHAN}} = J + c_{\text{H}}, \quad (13)$$

$$M_{\text{NaHAN}} = J = M_{\text{NaOH}}, \quad (14)$$

$$c_{\text{H}_2\text{An}} = M_{\text{H}_2\text{An}} - c_{\text{NaHAN}} = M_{\text{H}_2\text{An}} - J - c_{\text{H}}, \quad (15)$$

$$c_{\text{H}_2\text{An}} = M_{\text{H}_2\text{An}} \text{ (unneutralized)} - c_{\text{H}} = M_{\text{U}} - c_{\text{H}}, \quad (16)$$

$$M_{\text{U}} = M_{\text{H}_2\text{An}} - J, \quad (17)$$

for the titration to the first equivalent point. From the first equivalence point to end of the titration, the relations are

$$c_{\text{Na}_2\text{An}} = J - M_{\text{H}_2\text{An}} + c_{\text{H}}, \quad (18)$$

$$M_{\text{Na}_2\text{An}} = J - M_{\text{H}_2\text{An}}, \quad (19)$$

$$c_{\text{NaHAN}} = 2M_{\text{H}_2\text{An}} - J - c_{\text{H}}, \quad (20)$$

$$= M_{\text{H}_2\text{An}} - M_{\text{Na}_2\text{An}} - c_{\text{H}}, \quad (21)$$

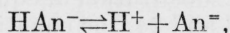
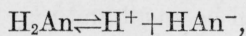
$$M_{\text{NaHAN}} = M_{\text{H}_2\text{An}} - M_{\text{Na}_2\text{An}}. \quad (22)$$

These relations hold only for the treatment of the acid groups each as a monobasic acid. In a later section it will be shown that overlapping occurs in the intermediate range of 0.85 to 1.15 mole added alkali.

In the above, stoichiometrical and ionic concentrations have been employed. They are self-explanatory. Stoichiometrical concentration means the concentration calculated from molecular weights and chemical reactions, while ionic concentration means the concentration of ions alone which are prevalent in the solution. Thus, if an electrolyte (like NaCl) is completely dissociated, the stoichiometrical and ionic concentrations are equal. However, for a weak acid like malonic, these concentrations differ. Thus, the stoichiometrical concentration of 0.10 *M* acid is 0.10 *M*, but its ionic concentration is equal to the hydrogen-ion concentration, since only H^+ and HAn^- ions are present and are of equal value. Similarly, along the titration curve, the ionic concentrations and stoichiometrical concentrations differ. For example, the ionic concentration of HAn^- ion is equal to the stoichiometrical value of $NaHAn$ formed by neutralization, plus H^+ , due to ionization of the acid into H^+ and HAn^- ions. Thus, the stoichiometrical and ionic values differ merely by a H^+ ion concentration (apparent in above equations). This treatment and distinction make it simpler to visualize the changing concentrations which occur during a titration in which there is a volume change. It is the ionic values that are employed in the calculations of the dissociation constants.

V. CALCULATION OF THE DISSOCIATION CONSTANTS

Malonic acid ionizes in two steps, thus:



and the law of mass action postulated by Guldberg and Waage [23] gives for these ionizations the respective constants

$$K_1 = \frac{a_H a_{HAn}}{a_{H_2An}} = \frac{c_H c_{HAn} f_H f_{HAn}}{c_{H_2An} f_{H_2An}} = K_1^c \frac{f_H f_{HAn}}{f_{H_2An}} \quad (23)$$

and

$$K_2 = \frac{a_H a_{An}}{a_{HAn}} = \frac{c_H c_{An} f_H f_{An}}{c_{HAn} f_{HAn}} = K_2^c \frac{f_H f_{An}}{f_{HAn}}, \quad (24)$$

where *a*, *f*, and *c* are the activity, the practical activity coefficient, and the concentration, in moles per liter, of the species denoted by subscripts, respectively. Guldberg and Waage's first postulation, as well as those followed by their contemporaries, was based entirely upon the *c* term and represented by K_1^c and K_2^c . Experiments, as well as theory, have shown, however, that the law of mass action defines the relation between products and reactants of a reaction in terms of activity rather than in concentration terms. The activity is equal to the product of the concentration and the activity coefficient as given in above equations. For dilute solutions (approximately 0.01 *N*) the activity coefficient is given as a function of the concentration by the theory of Debye and Hückel [3] in the form

$$\log f_1 = -\frac{2.954 \times 10^6}{2.3026 D^{3/2} T^{3/2}} z_1 z_2 \sqrt{\Sigma c_i z_i^2} = -A z_1^2 \sqrt{\mu}, \quad (25)$$

where D =solvent dielectric constant; T =absolute temperature; z =ionic charge; and 2.954×10^6 is equal to the numerical product of Boltzman's constant and the electronic charge. For solvent water, Wyman [24] obtained 78.54 for D . Since all these values are constant at a constant temperature and for a particular solvent, they may be grouped as one constant, A , whose numerical value is 0.506 at 25° C. For better average values, Guggenheim [25] employs an equation with higher powers and his equation gives

$$\log f_1 = -Az_1^2 \frac{\sqrt{\mu}}{1 + \sqrt{\mu}}, \quad (26)$$

in which electrolytes are treated essentially as though they have equal ionic parameters or ionic radii with an average value of 3.0 angstroms. For more concentrated solutions

$$\log f_1 = -Az_1^2 \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} + \beta\mu \quad (27)$$

This β term is a constant due to salt effects and is called the "salt coefficient." It arises from repulsive forces between ions in moderately concentrated solutions [26]. It is to be distinguished from the "ion-mole" coefficient, a solution parameter given by Acree and his collaborators [27], which comes into effect in more concentrated solutions where reaction between ions and neutral molecules may take place. If the "ion-mole" reaction, arising as it does from a triple-body collision, does take place in the dilute solutions under consideration here, it will be small and may be considered as a small part of the β term. Upon substitution of equation 27 for the activity coefficients in equations 23 and 24, the equations

$$\log K_1 = \log K_1^c + \log f_H - A \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} + \beta\mu, \text{ and} \quad (28)$$

$$\log K_2 = \log K_2^c + \log f_H - 4A \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} + A \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} + \beta'\mu - \beta\mu \quad (29)$$

are obtained where the value of f_{H_2An} is taken as unity, and β' term in equation 29 is a salt coefficient for dibasic salts and will be included subsequently in β . As may be seen, f_H is retained and evaluated from data on pure potassium chloride and pure hydrochloric acid by the MacInnes [21] assumption previously justified and described.*

Since β or the "salt coefficient" is unknown and may only be estimated [28], the term including β will be dropped. Then equations

$$\log K_1^a = \log K_1^c + \log f_H - A \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} \approx \log K_1, \text{ and} \quad (30)$$

$$\log K_2^a = \log K_2^c + \log f_H - 4A \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} + A \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} \approx \log K_2 \quad (31)$$

result, where K_1^a and K_2^a are the thermodynamic dissociation constants and equal the thermodynamic ionization constants in pure

* The expression for $\log f_1$ given by Debye-Hückel-Guggenheim is not employed for the evaluation of the activity coefficient of the hydrogen ion, owing to relative nature of the calculations for E_1 .

water, K_1 and K_2 , only if β or the "salt coefficient" is equal to zero. That this is nearly the case is evident from the constancy of K_1° and K_2° given in tables 2 and 3 as the ionic strength changes. Wangler [29] in some unpublished work on malic acid has found the "salt coefficients" to be of small magnitude.

Values of K_1° and K_2° are calculated from the values of the hydrogen-ion concentration given in tables 2 and 3 and of the ionic concentrations of sodium acid malonate and disodium malonate and concentration of unneutralized malonic acid. The latter three ionic concentrations are calculated from the stoichiometrical concentrations of table 1, the hydrogen-ion concentration and the equations 13, 18, 19, and 15 or 16, respectively. Thus in the calculations, ionic concentrations are employed and the sodium salts are taken to be completely dissociated [30]. Values calculated in this manner are given in column 7 of table 2.

The ionic strengths corresponding to the various ionic concentrations are equal to one-half the sum of each ion molality present in the solution multiplied by the square of its valence [31]. Thus, for the first part of the titration (curve A), the ionic strength, μ , is equal to $(2J+3c_H)/2$ and for the second part (curve D) to $(4J-M_{H_2An}+5c_H)/2$. Values of the ionic strengths are given in column 8 of table 2. K_1° and K_2° , the thermodynamic dissociation constants, are then calculated from the values of K_1° and K_2° and the ionic strengths by equations 30 and 31, in which A is equal to 0.506. Values thus obtained are given in the last column of table 2.

VI. CALCULATION OF THE INTERMEDIATE RANGE

In the preceding section the calculations for the first equivalent of NaOH (curve A) and for the second equivalent of NaOH (curve D) were made upon the postulation that each part of the titration could be calculated as though each acid group behaved like a monobasic acid, that is, that the neutralization of the first and second acid groups proceeded separately. That this is not true is evident from the variability in the values of K_1° , K_2° , K_1° , and K_2° in the middle portion of the titration (neighborhood of 24.86 ml of added alkali). This is also apparent from the ratio of the values of K_1° or K_1° obtained at the beginning of the titration, and of K_2° or K_2° obtained near the middle of the titration of the second group. This ratio is approximately 600, and it is well known [32] that a dibasic acid may be titrated as a monobasic acid within 1-percent error if this ratio is 5,000 and that the accuracy increases as the ratio becomes larger than 5,000. Since, in this case, K_1°/K_2° is only 600, an error much larger than 1 percent is introduced if the titration is made on the monobasic principle. In this case, the error is approximately 15 percent. A good value of K_1° is obtained until 85 percent of the first acid group has been neutralized. Beyond this point the constant increases rapidly, indicating the formation of Na_2An or the titration of the second group. After the stoichiometrical equivalence point has been reached, values of K_2° increase rapidly until 15 percent of the second group had been neutralized, and then good values of K_2° are obtained. Within this 30-percent range neutralization of both acid groups occurs simultaneously, very similar in principle to the titration of a mixed acid [33].

In order to calculate the various ionic concentrations within this range [33], the values for each concentration are solved by elimination of unknowns in the equations

$$M_{\text{NaOH}} + c_{\text{H}} = c_{\text{HAn}} + 2c_{\text{An}}, \quad (32)$$

which expresses solution neutrality, and

$$c_{\text{H}_2\text{An}} + c_{\text{An}} + c_{\text{HAn}} = M_{\text{H}_2\text{An}} \quad (33)$$

due to conservation of mass, together with the two equations 23 and 24. M and c have the same distinction as previously defined. Solving simultaneously, the concentration of the dimalonate ion is given by

$$c_{\text{An}} = \frac{M_{\text{H}_2\text{An}} K_1^c K_2^c}{c_{\text{H}}^2 + c_{\text{H}} K_1^c + K_1^c K_2^c}. \quad (34)$$

For this calculation, the average value of K_1^c from 0.00 to 21.10 ml added alkali and the average value of K_2^c from 28.35 to 45.83 ml added alkali were employed. The former is equal to 2.63×10^{-3} and the latter to 6.10×10^{-6} . With these values and known values of ($M_{\text{NaOH}} = J$) and $M_{\text{H}_2\text{An}}$ given in table 1, values of c_{An} are calculated. These values are given in column 5 of table 3. Values of the other ionic concentrations are obtained from these values of c_{An} and the same four equations, and are given in columns 6 and 7 of table 3. The ionic strengths are different from those calculated on the monobasic principle, and are larger in the first group titration and smaller in the second group titration, since the disodium malonate ion contributes more to the ionic strength than does sodium acid malonate, since the dibasic ion bears an ionic charge of 2. These new values of the ionic strength, calculated by $(4J - 2M_{\text{H}_2\text{An}} + 5c_{\text{H}})/2$ are given in column 8 of table 3. Values of K_1^c and K_2^c are then calculated for this 30-percent intermediate range as before in the monobasic treatment, and are listed in the last two columns of table 3. Three values of K_1^c and K_2^c calculated monobasically are also listed on each side of this 30-percent range. It should be emphasized again that E_D for this range is calculated by equation 10.

VII. DISCUSSION

It is apparent from equations 28 and 29 that the thermodynamic ionization constants, K_1 and K_2 , must vary as the concentration or ionic strength varies, and that this variation is a function of concentration, temperature, dielectric constant, repulsive forces due to presence of salt, and the ionic charge. This variation may be expressed by

$$K = \text{function } (c, T, D, \beta, z_i^2). \quad (35)$$

In the titration of a weak acid in which some un-ionized acid always remains, the dielectric constant of the solvent is also a variable, owing to change in the solvent as the amount of un-ionized acid varies. In this case, water is the solvent with a dielectric constant

[24] of 78.54. The dielectric constant of pure malonic acid is unknown, but it may be estimated from

$$\frac{D \text{ (malonic acid)}}{D \text{ (diethyl malonate)}} = \frac{D \text{ (tartaric acid)}}{D \text{ (diethyl tartrate)}}, \quad (36)$$

where the other three are known and taken from the International Critical Tables [34]. This gives a value of 67.0 for malonic acid at 25° C. Since the maximum concentration of undissociated malonic acid is 0.08514, the value of D for it would be 78.53, assuming a linear variation of the dielectric constant between pure water and pure malonic acid. The effect due to this is therefore negligible. It may be observed in table 2 that K_1^a varies from 2.10 (omitting the first point where no alkali has been added) to 2.05 at 20.10 cm³ added alkali. This small deviation (although a slight trend in K_1^a) indicates that β or the "salt coefficient" is nearly zero, and that K_1^a may be considered as approximately equal to K_1 , the true thermodynamic ionization constant at this salt concentration range. Moreover, the ionic strength varies only slightly from 0.02 to 0.05, and only a slight variation in the dissociation constant should be expected. However, it is to be emphasized that these values are the dissociation constants of malonic acid at a particular concentration of its sodium salts, and therefore differ from the constants which the acid would have in pure water, and known as the ionization constants. Since the concentration of salts is low these values of the dissociation constants are undoubtedly very close to the ionization constants. Since the slight variation shows an increase with decreasing ionic strength, the ionization constants are probably somewhat higher than these dissociation constants. The somewhat larger variation in K_2^a may be explained in like manner, and is more marked, owing to larger concentrations of salts and to the presence of two salts of unlike valence type, Na^+HAN^- and Na_2^+An^- . Since in practice and in application dissociation constants at a particular salt concentration are as important as the ionization constants in the absence of salts, these constants are of value in the interpretation of the properties of malonate solutions found in the oxidized portions of natural sugars and in malonate buffers. For the intermediate range, K_1^a shows the same slight increase as the ionic strength decreases, and K_2^a the same decrease with decreasing ionic strength.

The average of the values of K_1^a from 0.00 to 21.10 ml of added alkali is 2.06×10^{-3} , which also agrees well with the values obtained in the intermediate range. The average of the values of K_2^a from 28.35 to 41.85 ml of added alkali is 2.94×10^{-6} , which also agrees well with the values calculated for the intermediate range, except for the points where only a small amount of (An^-) ion is present.

Previous values reported in the literature [1], and the methods by which they were obtained, are given in table 4. The values for both constants are seen to show a marked divergence. As stated before, this divergence is partly due to neglect of interionic attraction corrections, and partly to assumption that the sodium salts of malonic acid are incompletely dissociated and possess the same equivalent conductances at the same equivalent concentration as do the sodium salts of other dibasic and monobasic acids. Britton's values were obtained

TABLE 4.—Primary and secondary dissociation constants of malonic acid obtained by various workers at 25° C

Observer	Method	$K_1 \times 10^3$	$K_2 \times 10^6$
The authors.....	pH titration curve (activity treatment).....	2.06	2.94
Burton.....	pH titration curve (classical treatment).....	2.07	3.89
Britton.....	pH titration curve (analytical treatment).....	2.11	4.45
White and Jones.....	Conductivity.....	1.63	-----
Salm.....	Colorimetric.....	1.6	-----
Berthelot.....	Conductivity.....	1.64	-----
Walden.....	do.....	1.63	-----
Ostwald.....	do.....	1.58	-----
Bethmann.....	do.....	1.71	-----
Vogel and Jeffery.....	Conductivity and the use of the parachor.....	1.397	-----
Datta and Dhar.....	CO ₂ absorption.....	-----	1.36
Chandler.....	Partition.....	-----	2.03
Chandler and McCoy.....	Conductivity.....	-----	2.1
Wegscheider.....	do.....	-----	10.0
Smith.....	Conductivity and sucrose inversion.....	-----	1.0

in a manner similar to the treatment presented herein, but no corrections were made for liquid-junction potentials nor for interionic attraction. The former raise the constants and the latter corrections lower them. For K_1 these are seen to counteract each other to a large extent, since all ions in solution bear a charge of 1, for with no corrections whatsoever, Britton obtained 2.11×10^{-3} , while in this work a value of 2.06×10^{-3} is obtained. For K_2 these conditions do not persist as the charges on the ions (H^+ , HAn , and An^-) differ, and Britton's value is high owing to the neglect of the interionic theory and liquid-junction corrections.

The low values obtained by the others are due, in the main, to the assumption of incomplete dissociation [30] of the sodium salts, a view generally accepted at the time of their determination, and also to the assumption that the degree of dissociation of these sodium salts was the same as for other similar basic sodium salts. To show that these low results are due to these assumptions and not so much to experimental differences, the following classical treatment has been incorporated here.

If α_1 is taken as the degree of dissociation of sodium acid malonate and α_2 as the degree of dissociation of disodium malonate, instead of assuming complete dissociation [30] of these salts, $\alpha_1 c_{NaHAn}$ is then substituted for c_{NaHAn} and $\alpha_2 c_{Na_2An}$ for c_{Na_2An} in the calculation of K_1° and K_2° . The value of α_1 is calculated from the ratio of the equivalent conductance of sodium acetate and the equivalent conductance of sodium acetate at infinite dilution, and α_2 from the same ratio for disodium tartrate, at the same equivalent concentration as present in the titrated solution. These salts were employed since their values [35] are known, and Noyes and Falk [36] and others [37] have shown that the basic salts have nearly the same equivalent conductance at equal equivalent concentrations. In table 5 a few values calculated in this manner are given as well as the new ionic strengths. These have been labeled with a subscript 0 to distinguish them from those obtained in the thermodynamic treatment. The subscript 0 has been chosen since this is the method Ostwald [38] and his contemporaries employed for the determination of ionization constants. It should be emphasized again in this connection that the ionization constants are expressed in terms of activity and not in concentration terms, and even though the α values have been employed, the result-

ant ionic concentrations must be multiplied by the activity coefficient, as was done in the calculations of K_1^a and K_2^a by equations 30 and 31 [39, 40, 41].

TABLE 5.—Classical Ostwald ionization constants and their values on the Debye-Hückel basis at a few points

0.1007 N NaOH	α_1	$K_1^o \times 10^3$	μ_0	$K_1^a \times 10^3$	0.1007 N NaOH	α_1	α_2	$K_2^o \times 10^6$	μ_0	$K_2^a \times 10^6$
ml					ml					
1.00	0.956	2.72	0.02312	2.08	28.35	0.869	0.803	5.30	0.05109	2.82
2.06	.940	2.64	.02343	2.05	29.35	.874	.787	5.41	.05276	2.86
3.21	.927	2.58	.02408	2.01	30.39	.878	.775	5.50	.05406	2.83
4.26	.917	2.55	.02490	1.99	31.85	.884	.767	5.63	.05686	2.80
5.11	.911	2.50	.02557	1.96	33.85	.890	.744	5.29	.05858	2.67
6.10	.904	2.48	.02649	1.89	35.85	.899	.730	5.21	.06026	2.61
11.08	.884	2.32	.03146	1.84	37.85	.906	.720	5.01	.06224	2.59
13.10	.878	2.27	.03344	1.80	39.85	.916	.711	4.98	.06347	2.47
15.10	.873	2.25	.03534	1.79	41.85	.925	.704	4.69	.06505	2.31
17.10	.868	2.24	.03710	1.79	42.85	.931	.700	4.59	.06558	2.25
19.10	.865	2.20	.03879	1.76	43.83	.936	.698	4.52	.06620	2.21
21.10	.861	2.27	.04034	1.83	44.83	.942	.695	4.39	.06670	2.14
22.10	.860	2.43	.04113	1.96	45.83	.949	.692	4.18	.06716	2.04

It may be seen that these values are lower than the values given in table 2 and closer to the conductivity values listed in table 4. Vogel and Jeffery's low value may be due to the postulation of equal conductivity for salts of the carboxyl and carbamyl groups, based upon their similar parachors.

These classical values are also seen to vary much more rapidly with the ionic strength and their average values for the same milliliter range, as was employed in the average for the thermodynamic constants, are 1.88×10^{-3} and 2.62×10^{-6} , respectively. These calculations illustrate the point for which they were intended, namely, that the low values reported in the literature are due in a large degree to the acceptance of incomplete dissociation and not so much to experimental differences. In addition, they were obtained with the use of α values, the determination of which depends upon the extrapolation to infinite dilution of the equivalent conductances. Since then, these methods of extrapolation have been greatly improved to include viscosity corrections [39], effect of Brownian movement on the ionic attraction between ions of unlike charge [40], and by the analytical treatment [41]. These corrections have not been made for the literature data, for in most cases the data did not warrant this treatment.

Since the classical values show much larger variation with ionic strength than do the thermodynamic values, and also depend upon the evaluation of α , which, at the best, can only be qualitative, the values given in tables 2 and 3 are considered to be the better. Also these values have been obtained by methods which are now generally accepted.

VIII. SUMMARY

The data for the electrometric titration of malonic acid 0.10 M by sodium hydroxide 0.1007 N at 25° C with the use of a hydrogen electrode and a saturated potassium chloride electrode are presented. Corrections for the liquid-junction potential between the titrated solution and the saturated potassium chloride are embodied in the

calculations. The pH titration curve is given and varies from 2 to 9 in pH for the solutions of malonic acid-sodium malonate salts.

The primary and secondary dissociation constants of malonic acid calculated on the activity basis, with corrections for interionic attraction, were found to be 2.06×10^{-3} and 2.94×10^{-6} , respectively. Brief discussions are given of the relation of these dissociation constants to the true ionization constants in pure water, and a comparison is made of these values with those calculated by classical methods used prior to the development of the Debye-Hückel theory.

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